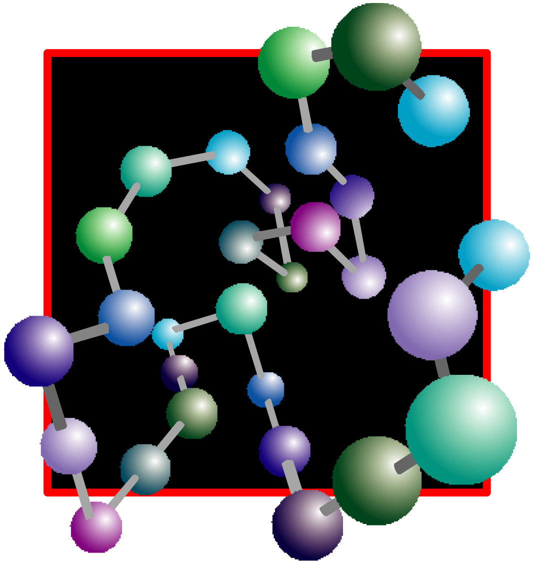
Introduction to polymer physics
Lecture 1

Boulder Summer School
July – August 3, 2012



A.Grosberg
New York University

Lecture 1: Ideal chains

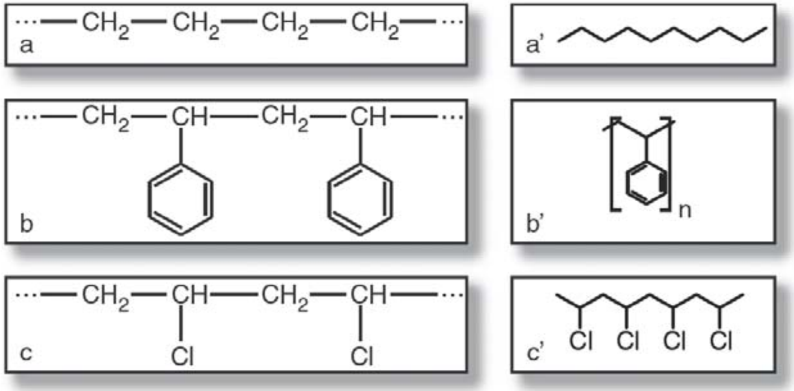
- **Course outline:**
- Ideal chains (Grosberg)
- Real chains (Rubinstein)
- Solutions (Rubinstein)
- Methods (Grosberg)
- Closely connected: interactions (Pincus), polyelectrolytes (Rubinstein) , networks (Rabin) , biopolymers (Grosberg), semiflexible polymers (MacKintosh)

- **This lecture outline:**
- Polymers and their uses
- Scales
- Architecture
- Polymer size and fractality
- Entropic elasticity
- Elasticity at high forces
- Limits of ideal chain

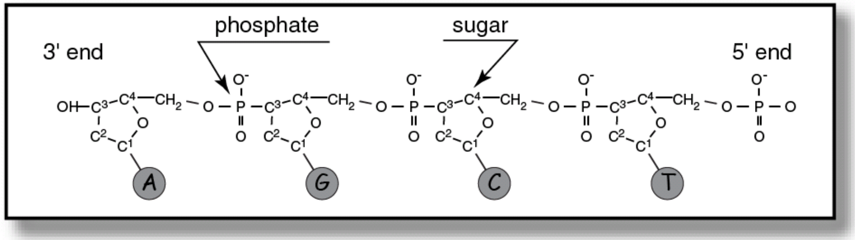
Polymer molecule is a chain:

- Polymeric from Greek *poly-merēs* having many parts; First Known Use: 1866 (Merriam-Webster);
- Polymer molecule consists of many elementary units, called monomers;
- Monomers – structural units connected by covalent bonds to form polymer;
- N number of monomers in a polymer, degree of polymerization;
- $M=N*m_{monomer}$ molecular mass.

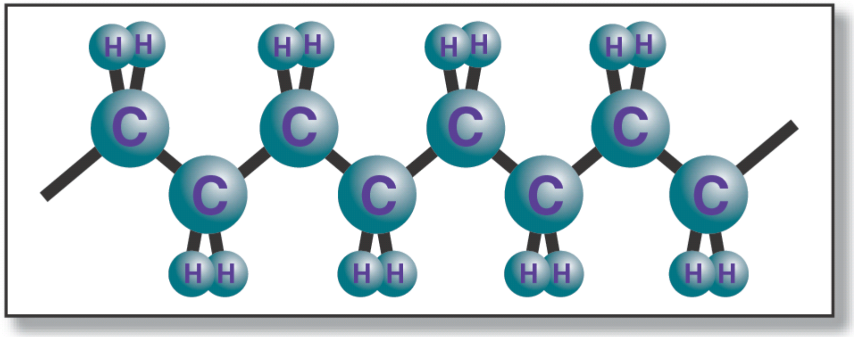
Examples: polyethylene (a), polysterene (b), polyvinyl chloride (c)…

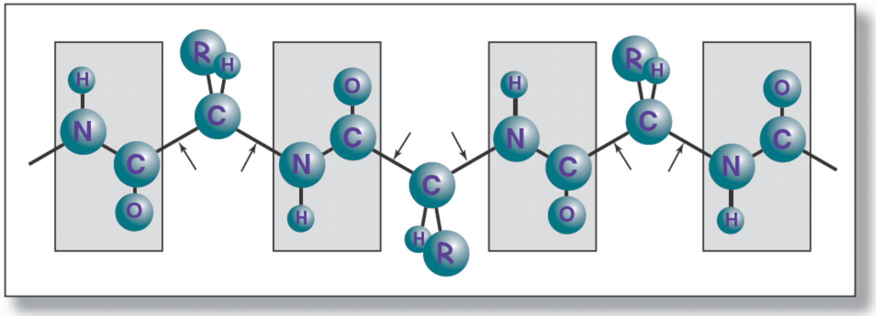


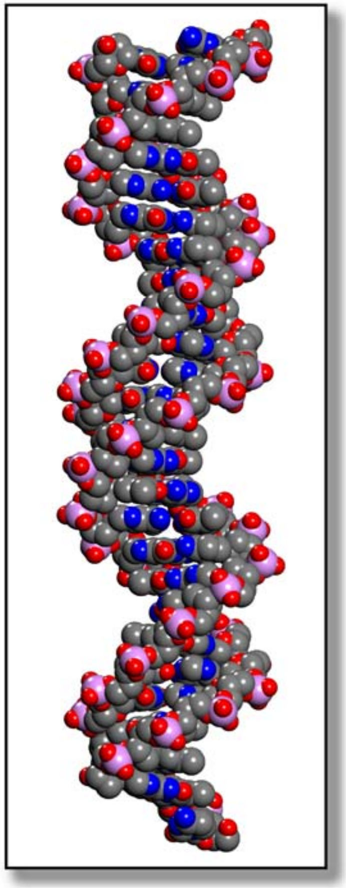
… and DNA



Another view:







Scales:

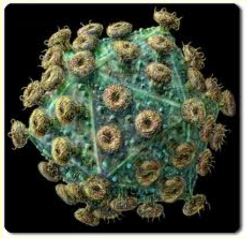
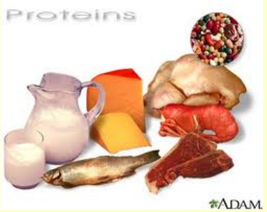
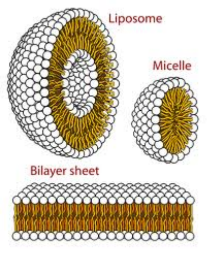
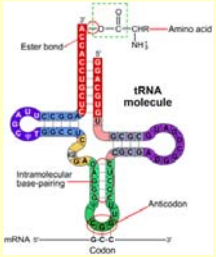
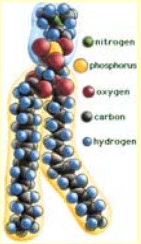
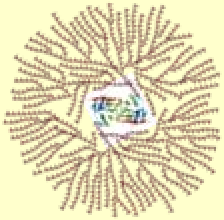
- $k_B T$=4.1 pN*nm at room temperature (24^{0}C)
- Breaking covalent bond: ~10000 K; **bonds are NOT in equilibrium.**
- "Bending" and non-covalent bonds compete with $k_B T$
- Monomer size b~Å;
- Monomer mass m – from 14 to ca 1000;
- Polymerization degree N~10 to 10^9;
- Contour length L~10 nm to 1 m.

Polymers in materials science

(e.g., alkane hydrocarbons $-(CH_2)-$)

# C atoms	1-5	6-15	16-25	20-50	1000 or more
@ 25°C and 1 atm	Gas	Low viscosity liquid	Very viscous liquid	Soft solid	Tough solid
Uses	Gaseous fuels	Liquid fuels and solvents	Oils and greases	Candles and coatings	Bottles…
Examples	Propane	Gasoline	Motor oil	Paraffin wax	Polyethylene
					

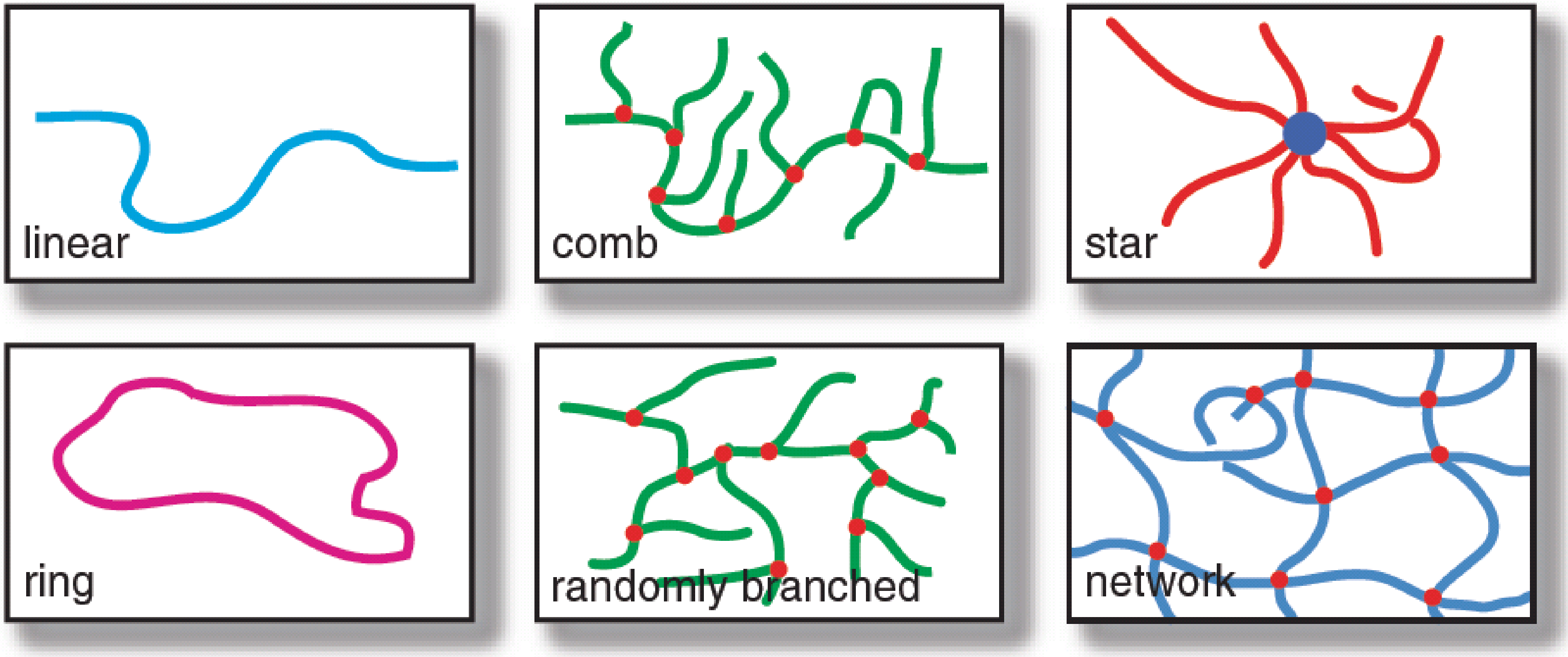
Polymers in living nature

	DNA	RNA	Proteins	Lipids	Polysaccharides
N	Up to 10^{10}	10 to 1000	20 to 1000	5 to 100	gigantic
Nice physics models	Bioinformatics, elastic rod, charged rod, helix-coil	Secondary structure, annealed branched, folding	Proteomics, random/designed heteropolymer,HP, funnels, ratchets, active brushes	Bilayers, liposomes, membranes	??? Someone has to start
Uses					
Molecule					

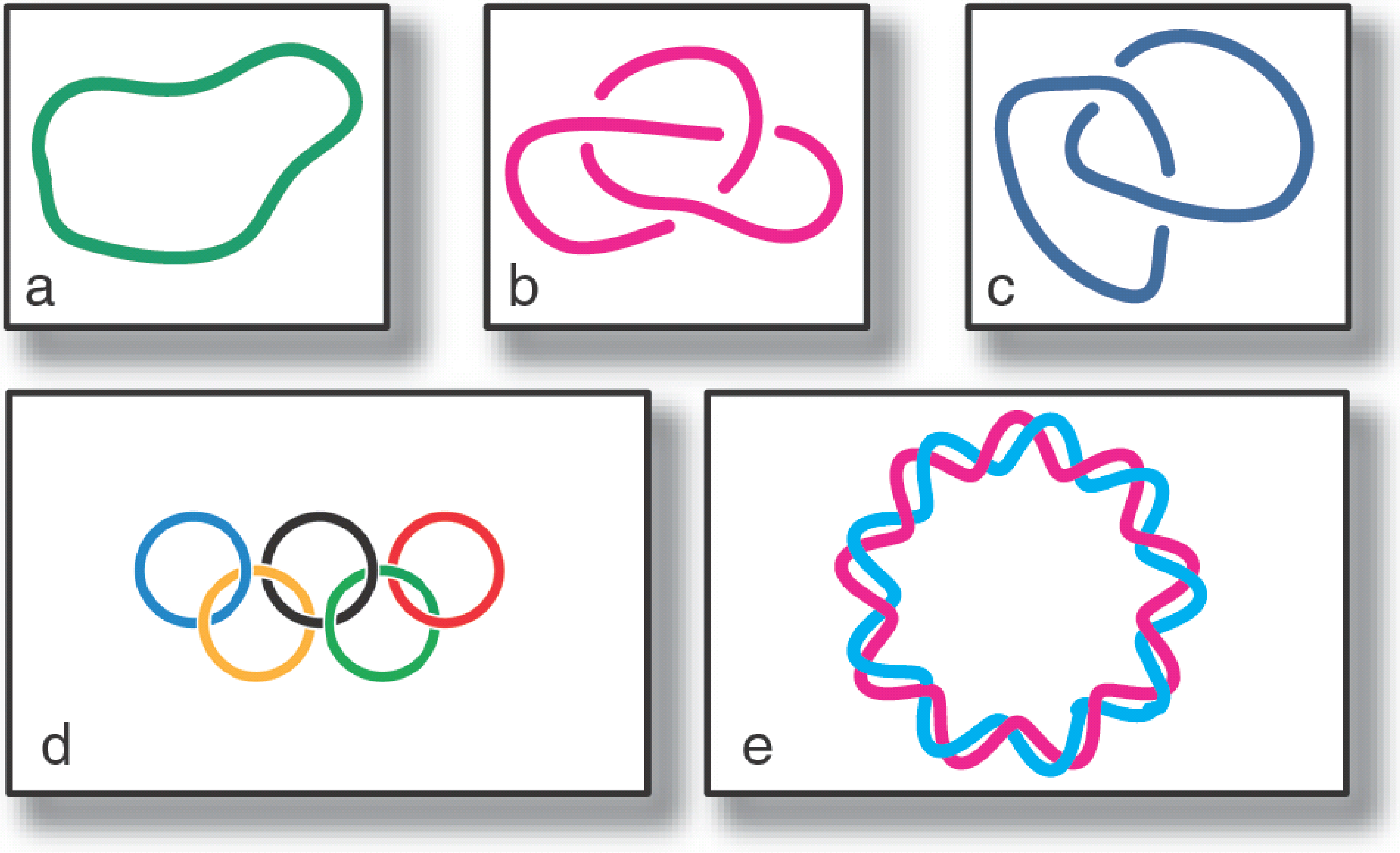
Polymer properties depend on…

- Chemical composition of a monomer;
- Degree of polymerization, N;
- Flexibility;
- Architecture;
- **Homo**polymer versus **hetero**polymer.

Architecture



Architecture cont'd



Homo- vs. Hetero

Homopolymer consists of monomers of just one sort:

A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

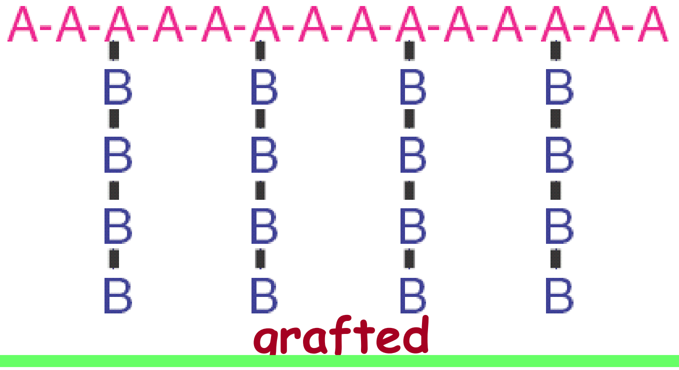
Heteropolymer (copolymer) has two or more monomer species:

A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B

alternating

A-A-A-B-B-A-B-B-B-B-A-B-A-A-B-A

random



grafted

Block-copolymers

A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B

diblock

A-A-A-A-B-B-B-B-B-B-B-A-A-A-A

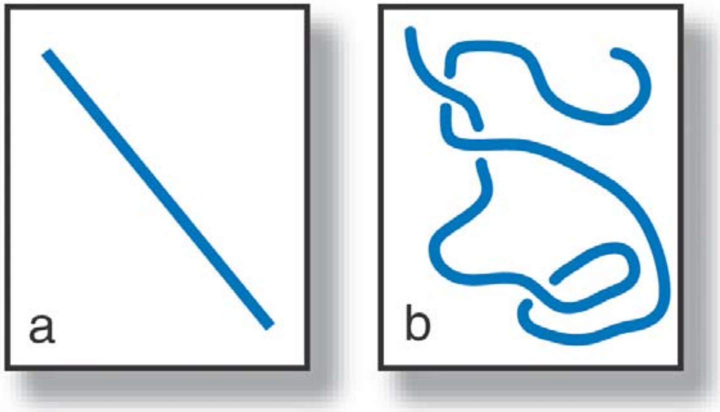
triblock

A-A-A-B-B-A-A-A-B-B-A-A-A-B-B-A-A-A-B-B

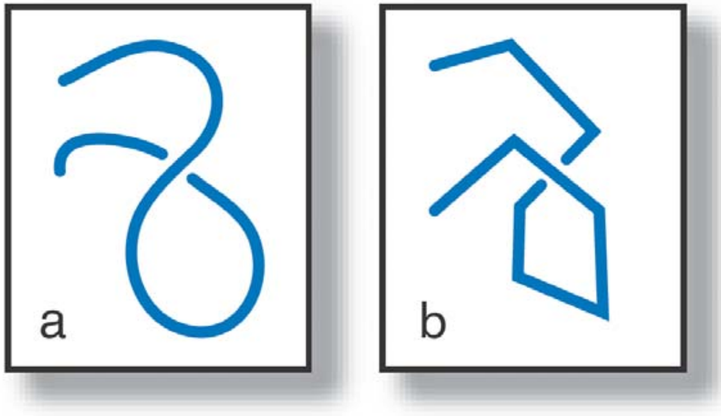
multiblock

Flexibility

- Sufficiently long polymer is never straight

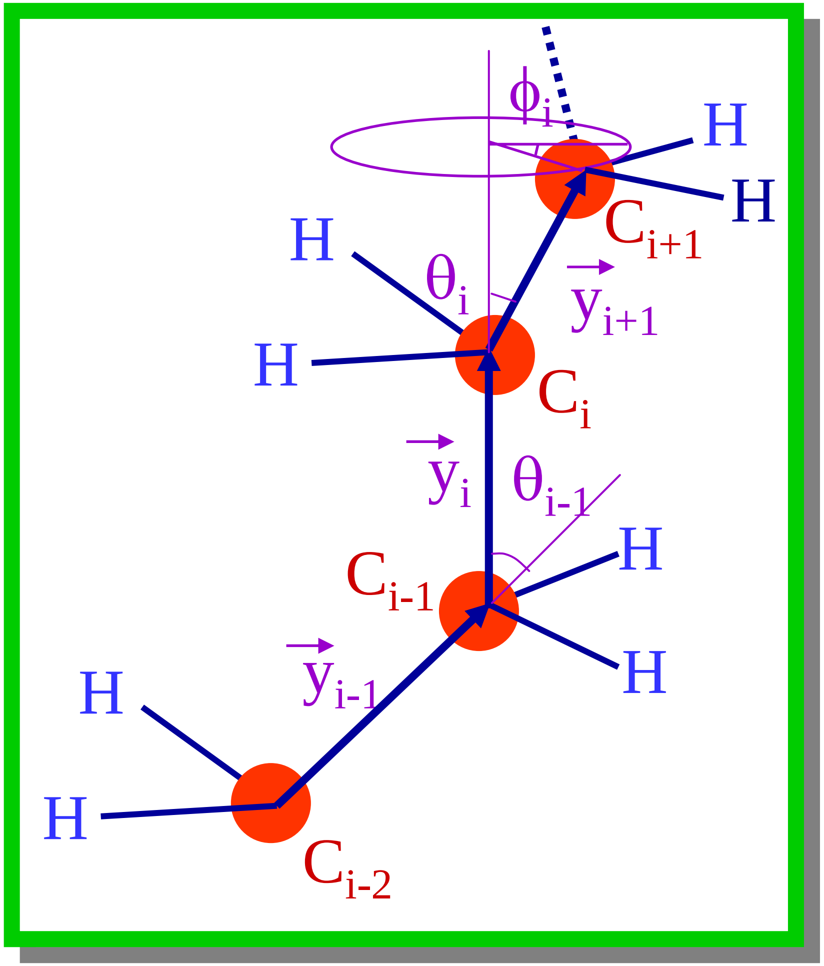


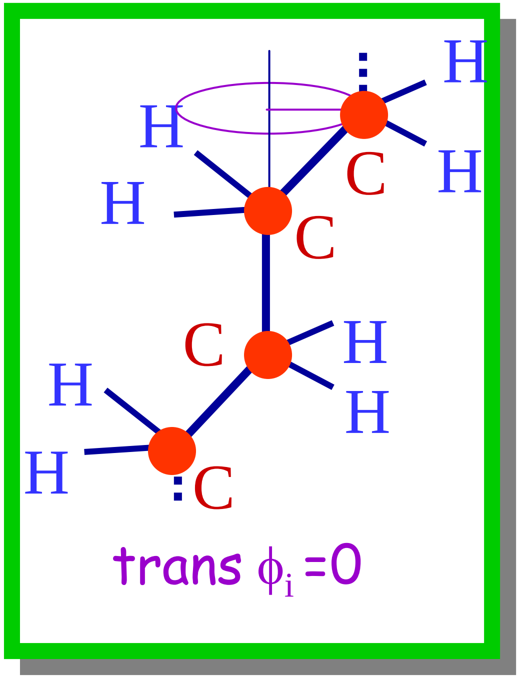
- Different polymers bend differently:



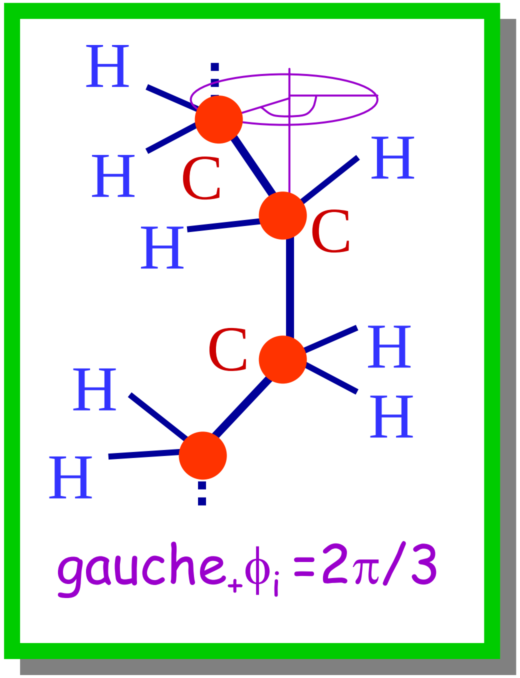
Rotation isomers:

Polyethylene: bond length $l \simeq 1.54 A$, tetrahedral angle $\theta \simeq 68^o$



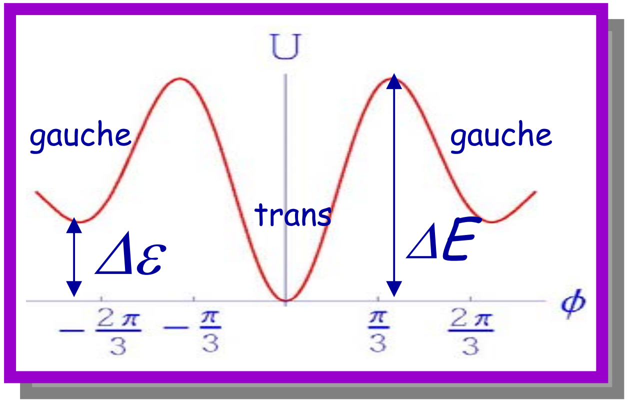


trans $\phi_i = 0$



gauche$_+$ $\phi_i = 2\pi/3$

$\Delta\varepsilon \sim k_B T$

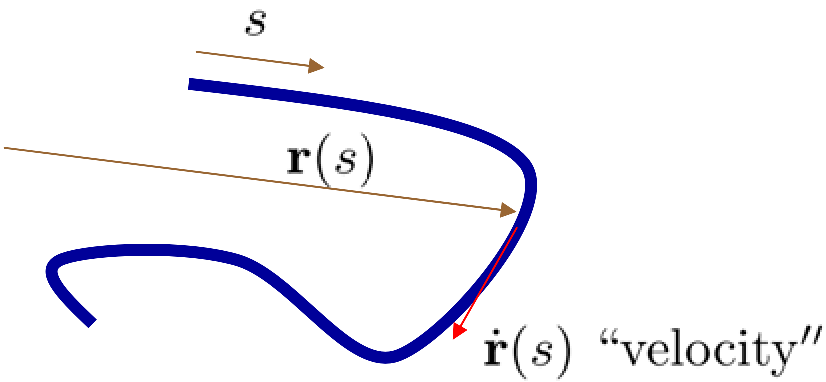


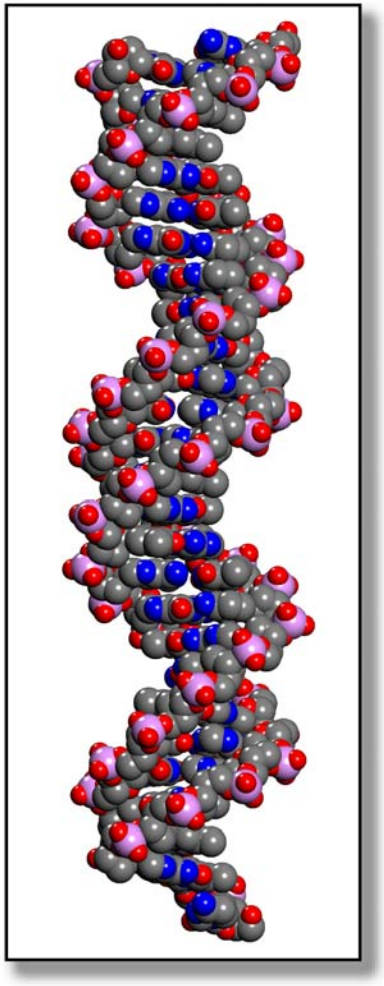
Torsion (measured in angle ϕ)- main source of polymer flexibility.

Elastic flexibility:

- Within one rotamer, $\Delta E \sim \phi^2$ – Hook's law.
- Many polymers have no freedom to explore rotational isomers, e.g., two strands.
- Elastic rod model:

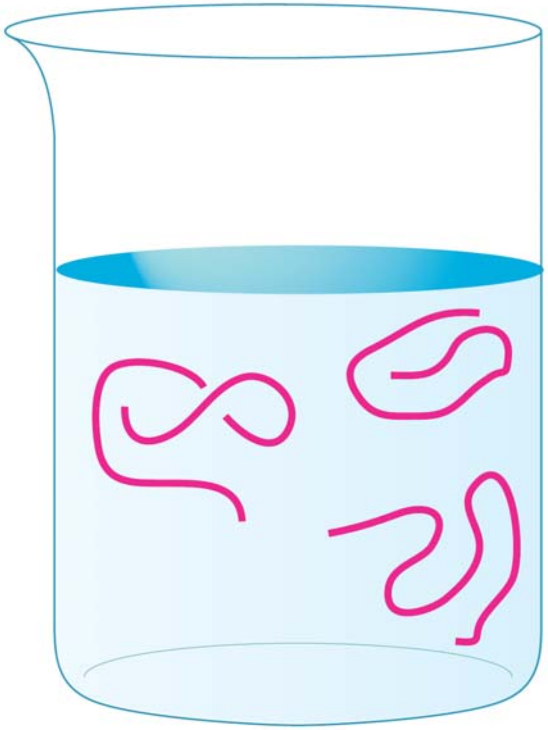
$$E = \int_0^L \left[\frac{1}{2}\kappa\ddot{\mathbf{r}}^2(s) + \frac{1}{2}\alpha\dot{\phi}^2(s)\right] ds$$





How much is polymer bent?

- How much is polymer bent?
- What is its size R, given N?
- Can we measure it?
- How/why is it important?
- How does it depend on conditions, e.g., temperature?



Polymer Size

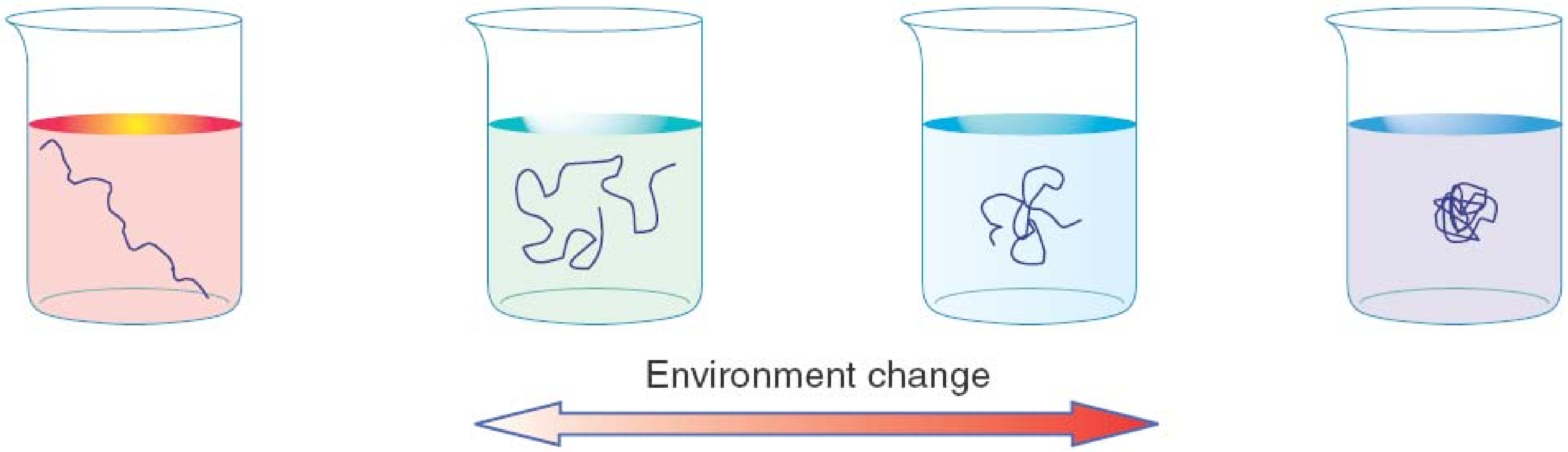
Monomer size b~0.1nm; Number of monomers N~10^2-10^{10};
Contour length L~10nm – 1m;
Depending on how much polymer is bent,
its overall size R varies widely and depends on solvent quality

Long-range repulsion $R \simeq L \simeq bN$

Good solvent $R \simeq bN^{3/5}$

θ-solvent $R \simeq bN^{1/2}$

Poor solvent $R \simeq bN^{1/3}$



R~1m

R~100mm

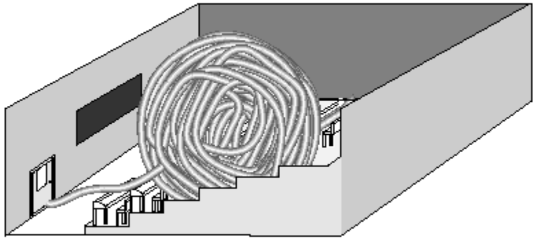
R~10mm

R~100nm

Astronomical Variations of Polymer Size

Increase monomer size by a factor of 10^8: b ~ 1cm; let $N=10^{10}$.

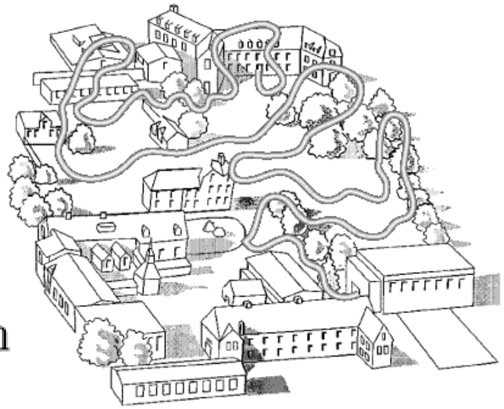
Poor solvent



$$R \simeq bN^{1/3} \approx 20\text{m}$$

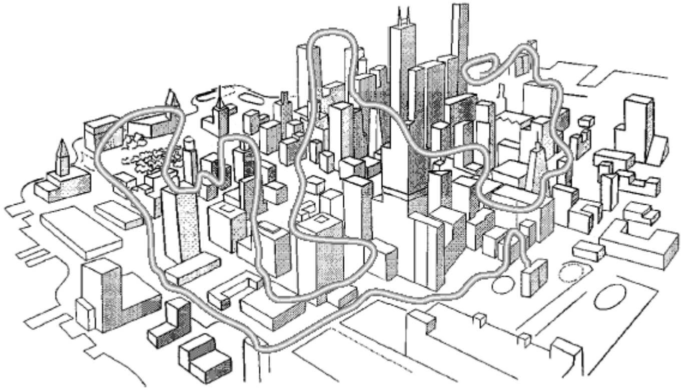
θ-solvent

$$R \simeq bN^{1/2} \approx 1\text{km}$$



Good solvent

$$R \simeq bN^{3/5} \approx 10\text{km}$$

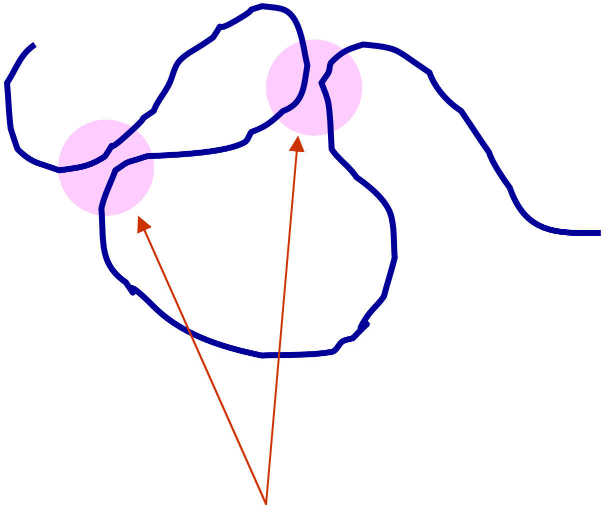


Long-range repulsion

$$R \simeq L \simeq bN \approx 10^5\ \text{km}$$

Ideal polymer vs. ideal gas

- Strong dependence of polymer size on environment/solvent conditions suggests a big role of interactions.
- Ideal polymer has no interactions between monomers, except between neighbors along the chain.
- Just like ideal gas may have all sorts of rotations and vibrations in the molecule, but no interactions between molecules.
- Like ideal gas is the most useful idealization in statistical mechanics, so is the ideal polymer.
- Ideal chains are good models for polymer melts, concentrated solutions, and dilute solutions at θ-temperature

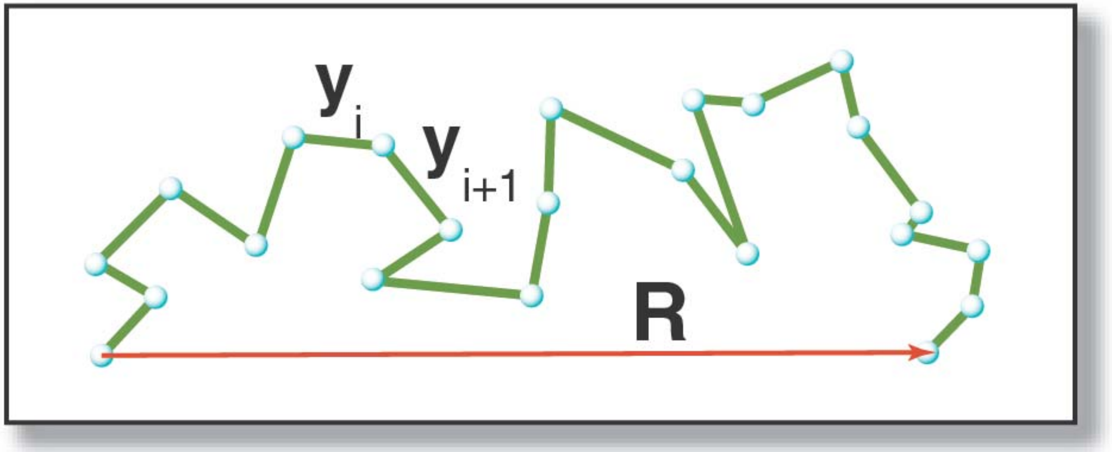


no interactions, the chain “does not see” itself

Ideal chain size

Ideal chain: no interactions between monomers if they are not neighbors along the chain, even if they approach one another in space.

Conformation of an ideal chain is fully specified by the set of bond vectors $\{y_i\}$



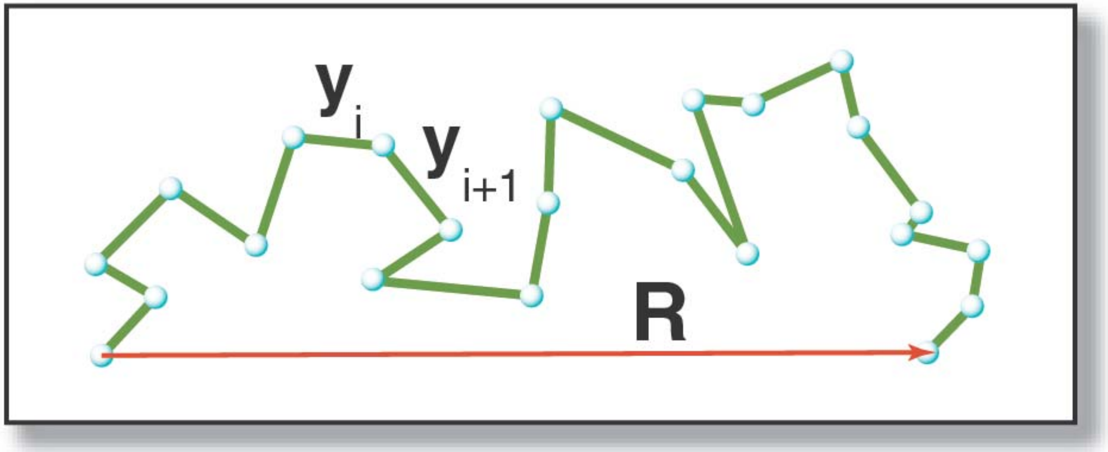
End-to-end vector of an ideal chain: $\mathbf{R} = \sum_{i=1}^{N} \mathbf{y}_i$

Averaged value of end-to-end *vector* is zero: $\langle \mathbf{R} \rangle = 0$, because $-\mathbf{R}$ is equally likely as $\mathbf{R}$

Ideal chain size: mean squared end-to-end distance

Ideal chain: no interactions between monomers if they are not neighbors along the chain, even if they approach one another in space.

Conformation of an ideal chain is fully specified by the set of bond vectors $\{y_i\}$



End-to-end vector of an ideal chain: $\mathbf{R} = \sum_{i=1}^{N} \mathbf{y}_i$

Since averaged value of end-to-end *vector* is zero: $\langle \mathbf{R} \rangle = 0$, to estimate the size we want to compute $\langle |\mathbf{R}| \rangle$ or $\langle \mathbf{R}^2 \rangle$

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle = \left\langle \left(\sum_{i=1}^{N} \mathbf{y}_i \right) \cdot \left(\sum_{j=1}^{N} \mathbf{y}_j \right) \right\rangle = \sum_{i,j=1}^{N} \langle \mathbf{y}_i \cdot \mathbf{y}_j \rangle = l^2 \sum_{i,j=1}^{N} \langle \cos\theta_{ij} \rangle$$

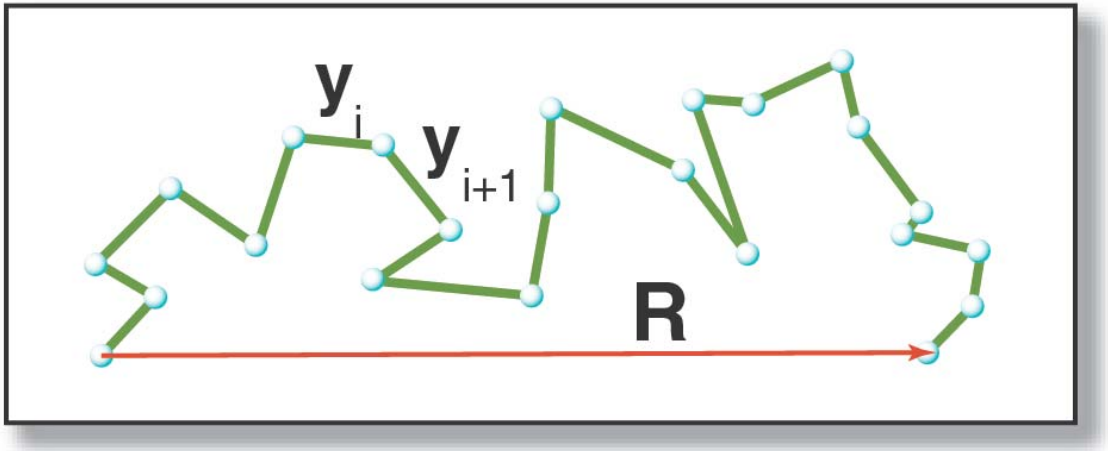
Freely-jointed chain or lattice model:

$$\langle \cos\theta_{ij} \rangle = 0 \text{ except when } i = j \quad \Longrightarrow \quad \langle \mathbf{R}^2 \rangle = N l^2$$

Ideal chain size: mean squared end-to-end distance

For ideal chains, one can show that there are no long-range correlations between bond directions:

$$\lim_{|i-j|\to\infty} \langle \cos\theta_{ij} \rangle = 0$$



$$C_i' = \sum_{j=1}^{N} \langle \cos\theta_{ij} \rangle \text{ rapidly converges at large } N$$

$$\langle \mathbf{R}^2 \rangle = l^2 \sum_{i,j=1}^{N} \langle \cos\theta_{ij} \rangle = l^2 \sum_{i=1}^{N} C_i' = C_N N l^2 \simeq C_\infty N l^2$$

For example, freely-rotating chain: $C_\infty = \frac{1+\cos\theta}{1-\cos\theta}$

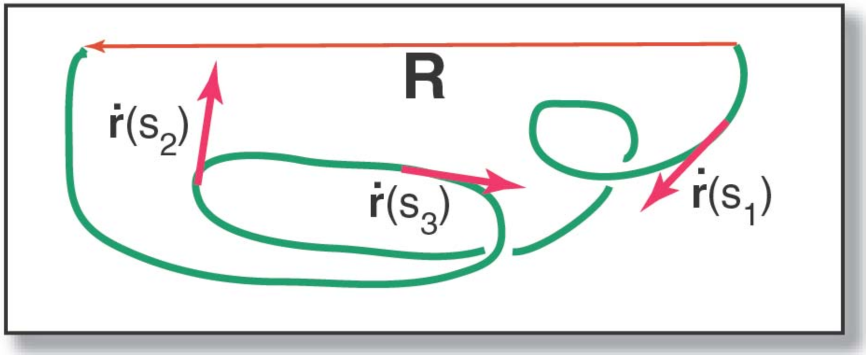
Specific flexibility mechanism (rotational isomers etc) is hidden in characteristic ratio C_∞;

see P.Flory, Statistical Mechanics of Chain Molecules

Ideal chain size: worm-like chain

(Kratky and Porod model)

$$\mathbf{R} = \sum_{i=1}^{N} \mathbf{y}_i \implies \mathbf{R} = \int_0^L \dot{\mathbf{r}}(s)ds$$



Key argument:

$$\langle \cos\theta_{s_1,s_3}\rangle = \langle \cos\theta_{s_1,s_2}\rangle \langle \cos\theta_{s_2,s_3}\rangle$$

Proof: consider $\dot{\mathbf{r}}_1 \cdot \dot{\mathbf{r}}_3 = \dot{\mathbf{r}}_1^{\perp}\dot{\mathbf{r}}_3^{\perp} + \dot{\mathbf{r}}_1^{||} \cdot \dot{\mathbf{r}}_3^{||}$, where parallel and perpendicular components are taken with respect to $\dot{\mathbf{r}}_2$. Perpendicular components vanish upon averaging.

Consequence: $\langle \cos\theta(s-t)\rangle = e^{-|s-t|/l}$

$$\langle \mathbf{R}^2\rangle = \int_0^L \int_0^L \langle \dot{\mathbf{r}}(s)\cdot\dot{\mathbf{r}}(t)\rangle\, dsdt = \int_0^L \int_0^L \langle \cos\theta(s-t)\rangle\, dsdt = \int_0^L \int_0^L e^{-|s-t|/l} dsdt$$

$$\langle \mathbf{R}^2\rangle = 2l^2\left[\tfrac{L}{l} - 1 + e^{-L/l}\right] = \begin{cases} L^2 & \text{if} \quad L \ll l \\ 2Ll & \text{if} \quad L \gg l \end{cases}$$

Problem: relate length l to rigidity constant κ in $\Delta E = \int_0^L \frac{1}{2}\kappa \ddot{\mathbf{r}}^2(s)ds$.

Universal description of ideal polymer

Construct **equivalent freely jointed chain** with the same mean squared end-to-end distance $\langle R^2 \rangle$ and the same contour length L as actual polymer. It consists of N effective, or Kuhn, segments, each of length b, such that:

For chain of n bonds of length l each:

$$\begin{aligned} \langle \mathbf{R}^2 \rangle = Nb^2 &= C_\infty n l^2 \\ Nb &= nl \end{aligned}$$

Kuhn length and #of effective segments are

$$\begin{aligned} b &= C_\infty l \\ N &= n/C_\infty \end{aligned}$$

Worm-like chain, total length L, persistence l:

$$\begin{aligned} \langle \mathbf{R}^2 \rangle = Nb^2 &= 2Ll \\ Nb &= L \end{aligned}$$

Kuhn length and #of effective segments are

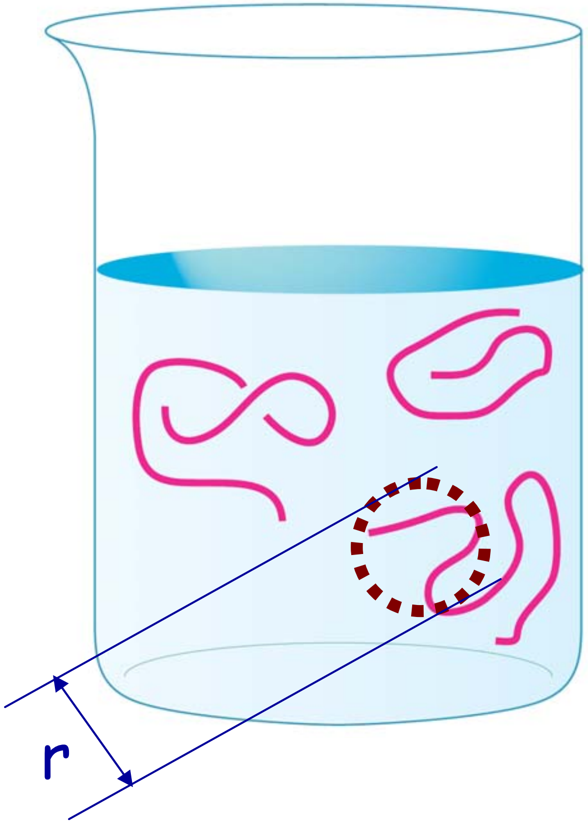
$$\begin{aligned} b &= 2l \\ N &= L/2l \end{aligned}$$

Equivalent freely jointed chain differs from the actual polymer on length scales of Kuhn segment b or smaller, but has the same physical properties on large scales

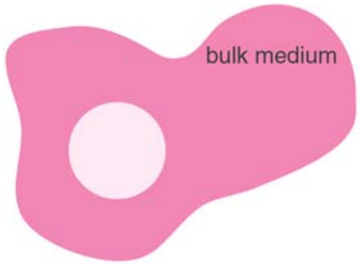
Reverse the question of polymer size:

how many monomers are there within radius r?

- If r is greater than Kuhn segment, r>b, then sub-coil of g monomers has size $R(g) \sim g^{1/2}b$;
- Therefore, within radius r we expect $m(r) \sim (r/b)^2$ monomers.

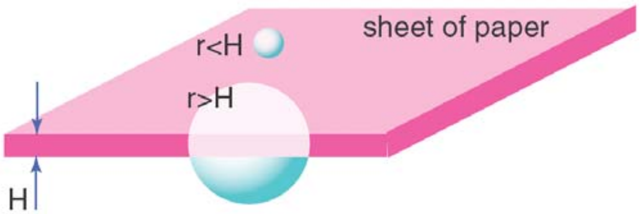


Counting "atoms" in regular objects



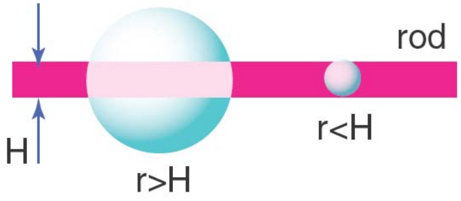
$$m(r) = \frac{4\pi}{3} r^3$$

m~r^3
for 3D object



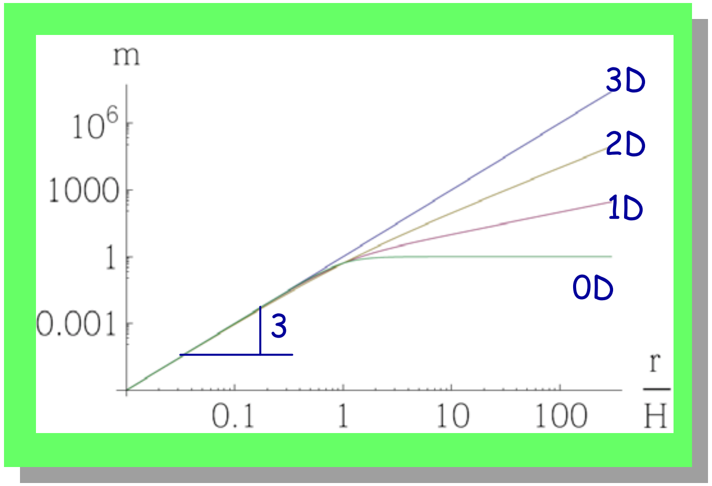
$$m(r) = \begin{cases} \frac{4\pi}{3} r^3 & \text{if} \quad r < H \\ \pi r^2 & \text{if} \quad r \gg H \end{cases}$$

m~r^2
for 2D object

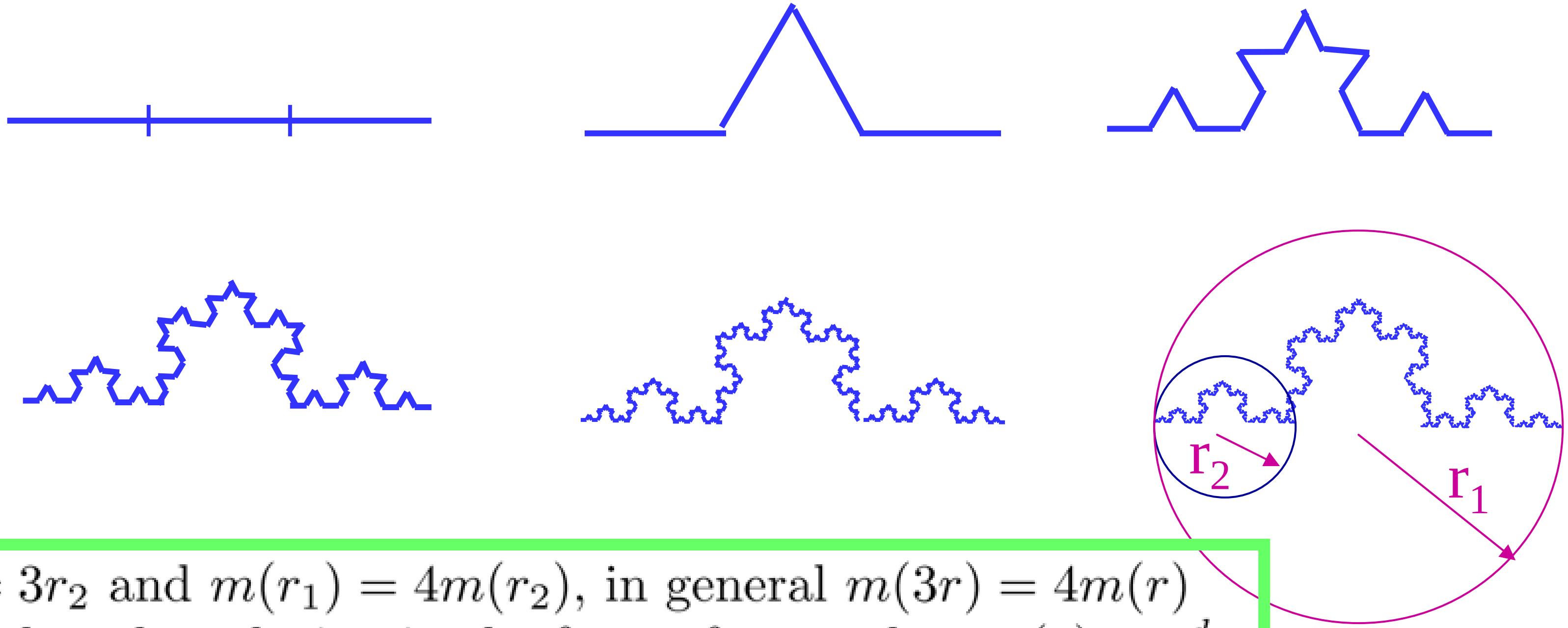


$$m(r) = \begin{cases} \frac{4\pi}{3} r^3 & \text{if} \quad r < H \\ 2r & \text{if} \quad r \gg H \end{cases}$$

m~r^1
for 1D object



Koch curve: example of a fractal



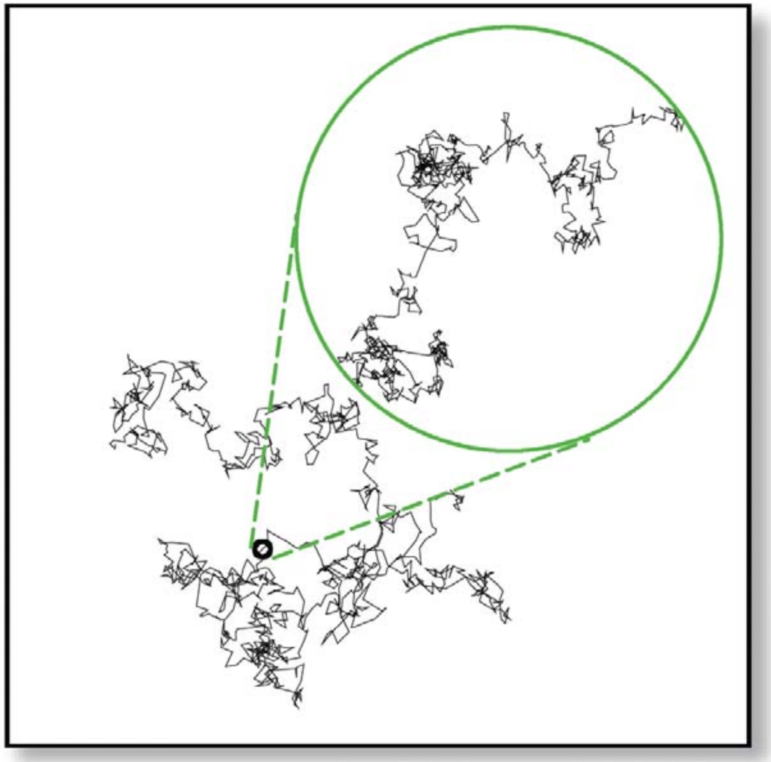
$r_1 = 3r_2$ and $m(r_1) = 4m(r_2)$, in general $m(3r) = 4m(r)$
This has the solution in the form of power law $m(r) \sim r^{d_f}$,
with $3^{d_f} = 4$ or $d_f = \frac{\ln 4}{\ln 3} \approx 1.26$.

$m \sim r^{df}$

d_f - fractal dimension

We can either increase "observation field" r, or
decrease the size of elementary "atom"

Polymeric fractals



For ideal chain, $m(r) \sim (r/b)^2$; that means, ideal polymer has fractal dimension $d_f=2$.

Scaling exponent $\nu=1/d_f=1/2$ for ideal polymer.

We will see later that in a good solvent $d_f=5/3$ and $\nu=3/5$

Ideal coil can be viewed as N/g blobs of g segments each. Blob size is $x \sim bg^{1/2}$, therefore $R \sim bN^{1/2} \sim x(N/g)^{1/2}$

Problem: consider polymer adsorbed on a 2D plane. What are the consequences of the fact that $d_f=D$?

Radius of gyration

End-to-end distance is difficult to measure (and it is ill defined for, e.g., rings or branched polymers). Better quantity is gyration radius:

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}\left(\mathbf{R}_i - \mathbf{R}_{\mathrm{cm}}\right)^2$$

Where position vector of mass center is

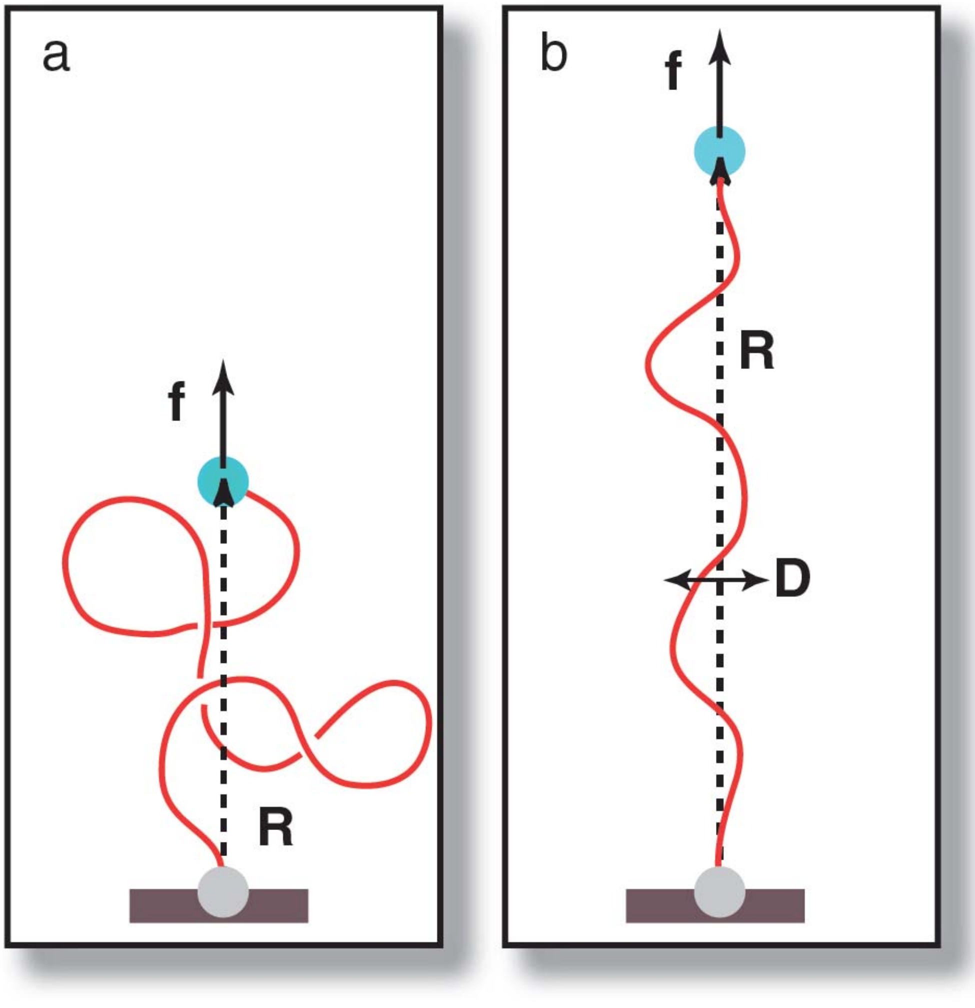
$$\mathbf{R}_{\mathrm{cm}} = \frac{1}{N}\sum_{i=1}^{N}\mathbf{R}_i$$

There is theorem (due to nobody lesser than Lagrange) which says that

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\mathbf{R}_i - \mathbf{R}_j\right)^2$$

Exercises: (1) Prove Lagrange theorem; (2) Prove that for ideal linear chain $R_g^2 = Nb^2/6$; (3) Prove that for ideal ring $R_g^2 = Nb^2/12$

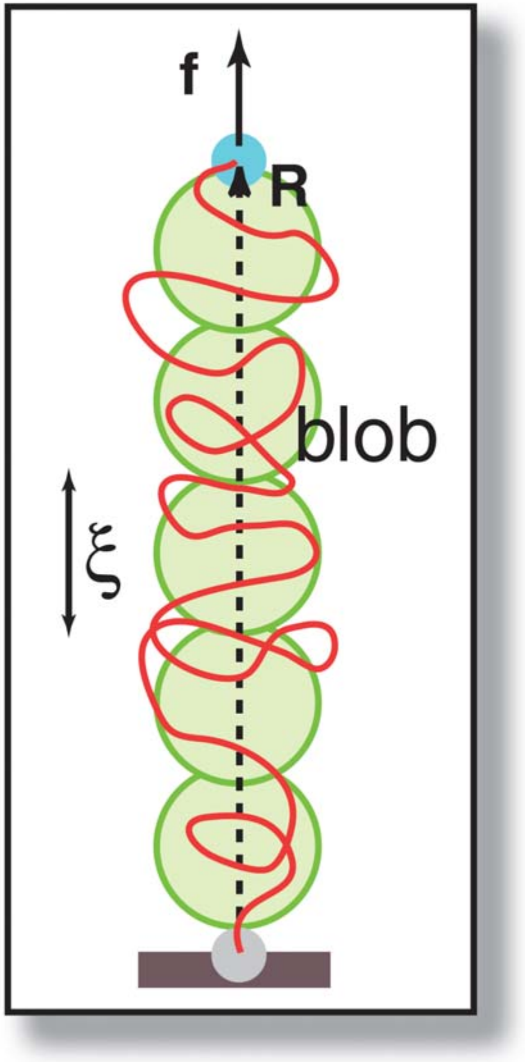
Entropic elasticity

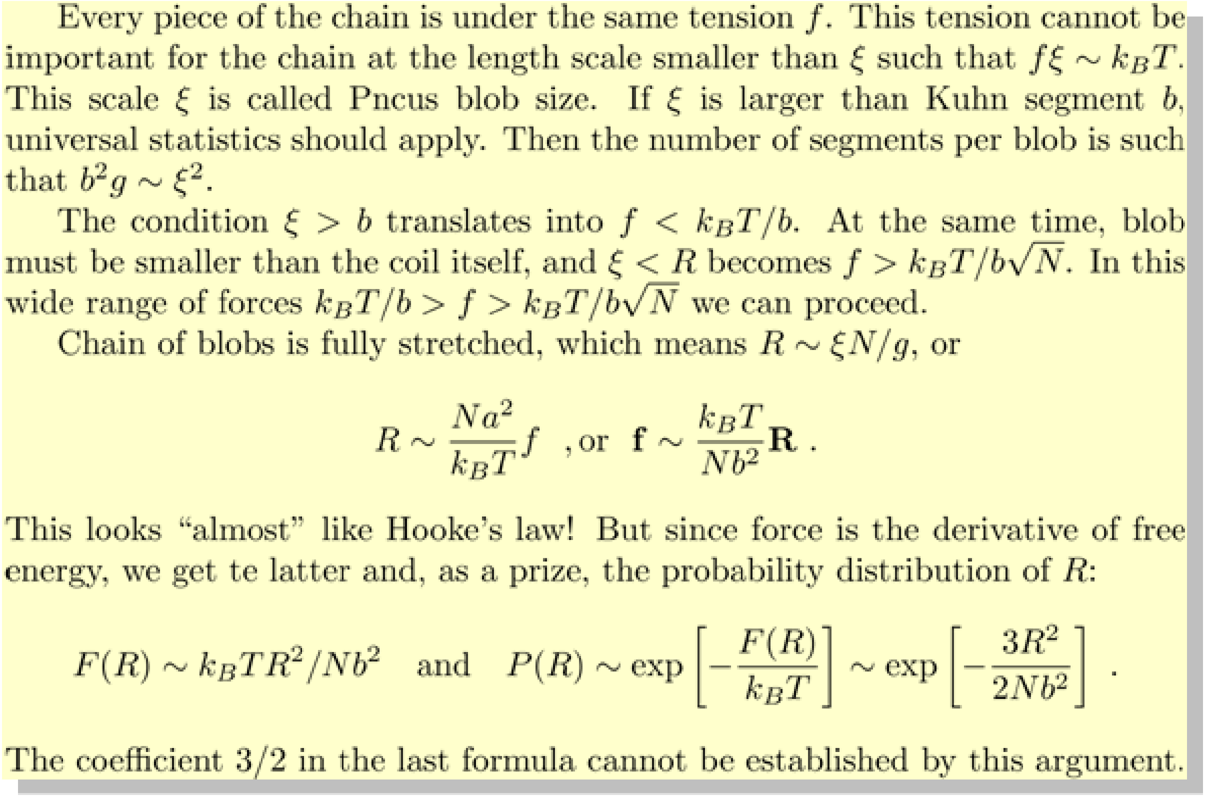


Optical tweezers experiment

How much force should we apply to achieve end-to-end distance R?

Pincus blob argument





Every piece of the chain is under the same tension f. This tension cannot be important for the chain at the length scale smaller than ξ such that $f\xi \sim k_BT$. This scale ξ is called Pncus blob size. If ξ is larger than Kuhn segment b, universal statistics should apply. Then the number of segments per blob is such that $b^2 g \sim \xi^2$.

The condition $\xi > b$ translates into $f < k_BT/b$. At the same time, blob must be smaller than the coil itself, and $\xi < R$ becomes $f > k_BT/b\sqrt{N}$. In this wide range of forces $k_BT/b > f > k_BT/b\sqrt{N}$ we can proceed.

Chain of blobs is fully stretched, which means $R \sim \xi N/g$, or

$$R \sim \frac{Na^2}{k_BT} f \quad \text{, or} \quad \mathbf{f} \sim \frac{k_BT}{Nb^2}\mathbf{R} \; .$$

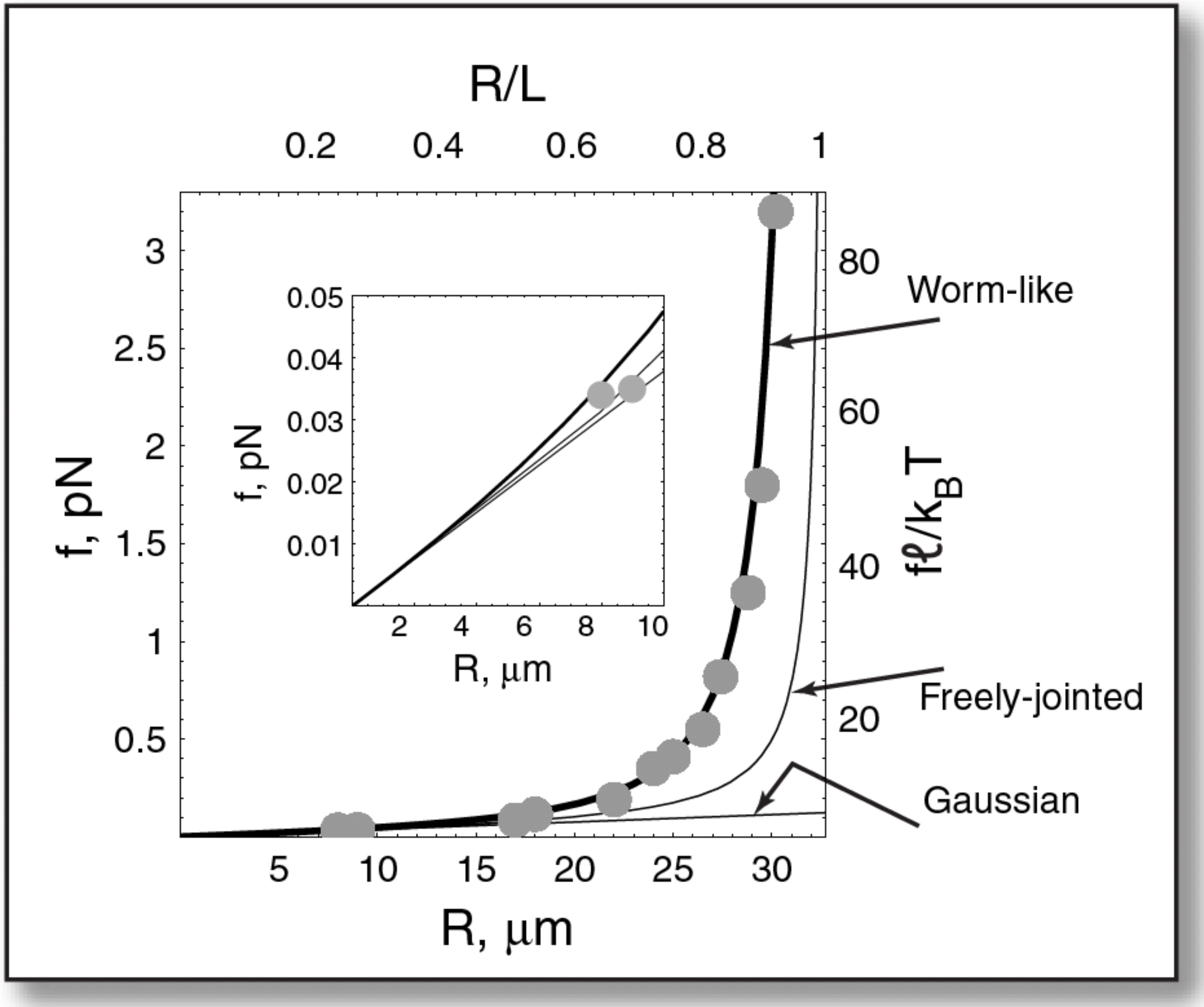
This looks "almost" like Hooke's law! But since force is the derivative of free energy, we get te latter and, as a prize, the probability distribution of R:

$$F(R) \sim k_BTR^2/Nb^2 \quad \text{and} \quad P(R) \sim \exp\left[-\frac{F(R)}{k_BT}\right] \sim \exp\left[-\frac{3R^2}{2Nb^2}\right] \; .$$

The coefficient 3/2 in the last formula cannot be established by this argument.

Gauss distribution of R follows directly from Central Limit Theorem

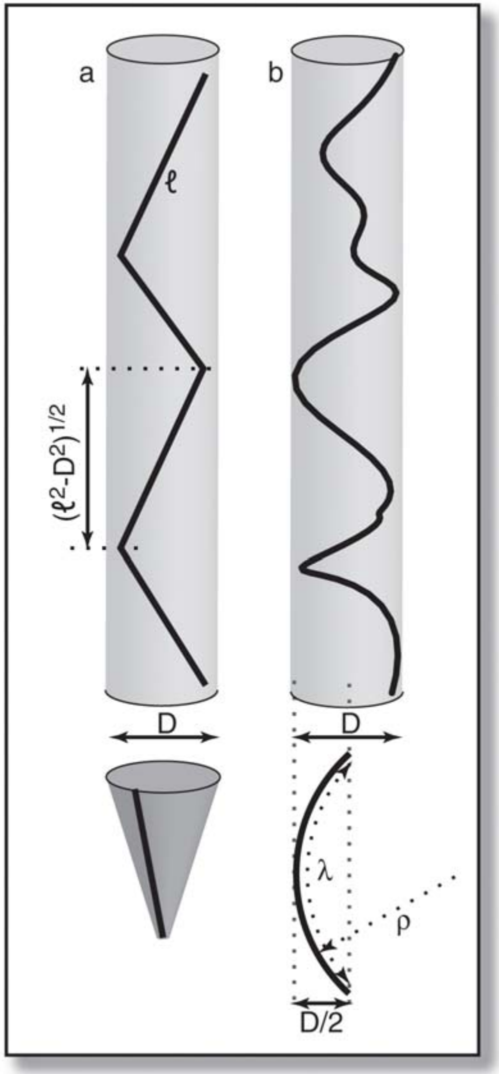
What if we pull harder?



Gaussian theory is satisfactory only up to about 0.1pN

S. Smith, L. Finzi, C. Bustamante, \Direct Mechanical Measurements of the Elasticity of Single DNA Molecules by using Magnetic Beads", Science, v. 258, n. 5085, p. 1122, 1992.

Non-universal elasticity at higher forces



Freely-jointed: Entropic price of confining one segment into a tube is about $k_B \ln(D^2/\ell^2)$, or $\Delta S = Nk_B \ln(D^2/\ell^2)$. How is D related to end-to-end distance R? For each segment, its projection along the tube axis is $\sqrt{\ell^2 - D^2} \simeq \ell - D^2/2\ell$ (since $D \ll \ell$). Therefore, $R \simeq N\left(\ell - D^2/2\ell\right) = L - LD^2/2\ell^2$. Then

$$\Delta F \sim -k_B T \ln\left(1 - \frac{R}{L}\right) \quad \text{and} \quad f \sim \frac{k_B T}{L-R} .$$

Worm-like: Curvature radius ρ of the arc is about $\rho \sim \lambda^2/D$. Bending energy of the arc $E_{\text{bend}} \sim k_B T b \lambda/\rho^2$ being about $k_B T$ yields Odijk length:

$$\lambda \sim b^{1/3} D^{2/3} .$$

Worm-like chain hits the tube walls more frequently, in more places, than freely-jointed chain, since $\lambda \ll b$. End-to-end distance R is geometrically related to λ: $R \simeq L - LD^2/2\lambda^2$, or $R - L \simeq -L\lambda/b$.

Confinement entropy is of order unity per Odijk length:

$$\Delta F \sim -k_B T \frac{L^2}{(L-R)b} \quad \text{and} \quad f \sim \frac{k_B T L^2}{(L-R)^2 b} .$$

From Langevin to Marko-Siggia

- Exact formula for freely-jointed chain:

$$R = N\ell\left(\frac{e^{\xi}+e^{-\xi}}{e^{\xi}-e^{-\xi}} - \frac{1}{\xi}\right)$$

where

$$\xi = \frac{f\ell}{k_B T}$$

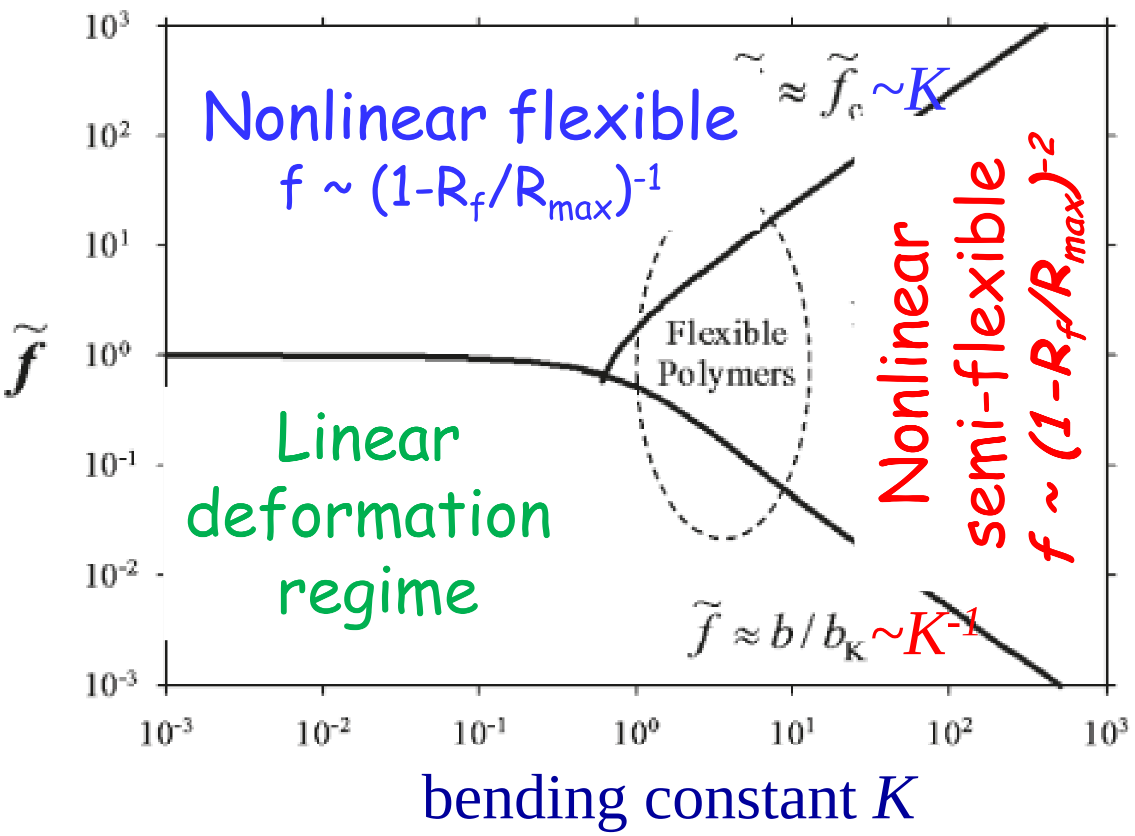
- Very accurate formula for worm-like chain:

$$f = \frac{k_B T}{2b}\left[\frac{L^2}{(L-R)^2} - 1 + \frac{4R}{L}\right]$$

Compare: Einstein and Debye theories of heat capacity of a solid

Chains Get Softer Under Tension

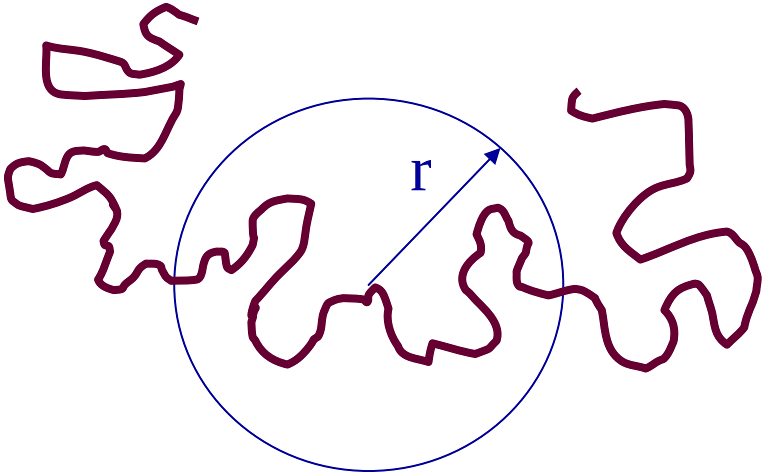
Macromolecules **2010**, *43*, 9181–9190



Linear deformation regime ends at **$f \sim k_BT /b$.**

<u>Problem:</u> Why is there a cross-over from semi-flexible (worm-like) chain to flexible (freely-jointed) chain with increasing tension at $f_c \sim k_BT\ K/l$?

Pair Correlations of an Ideal Chain



Number of monomers within range r

$$m \approx \left(\frac{r}{b}\right)^2$$

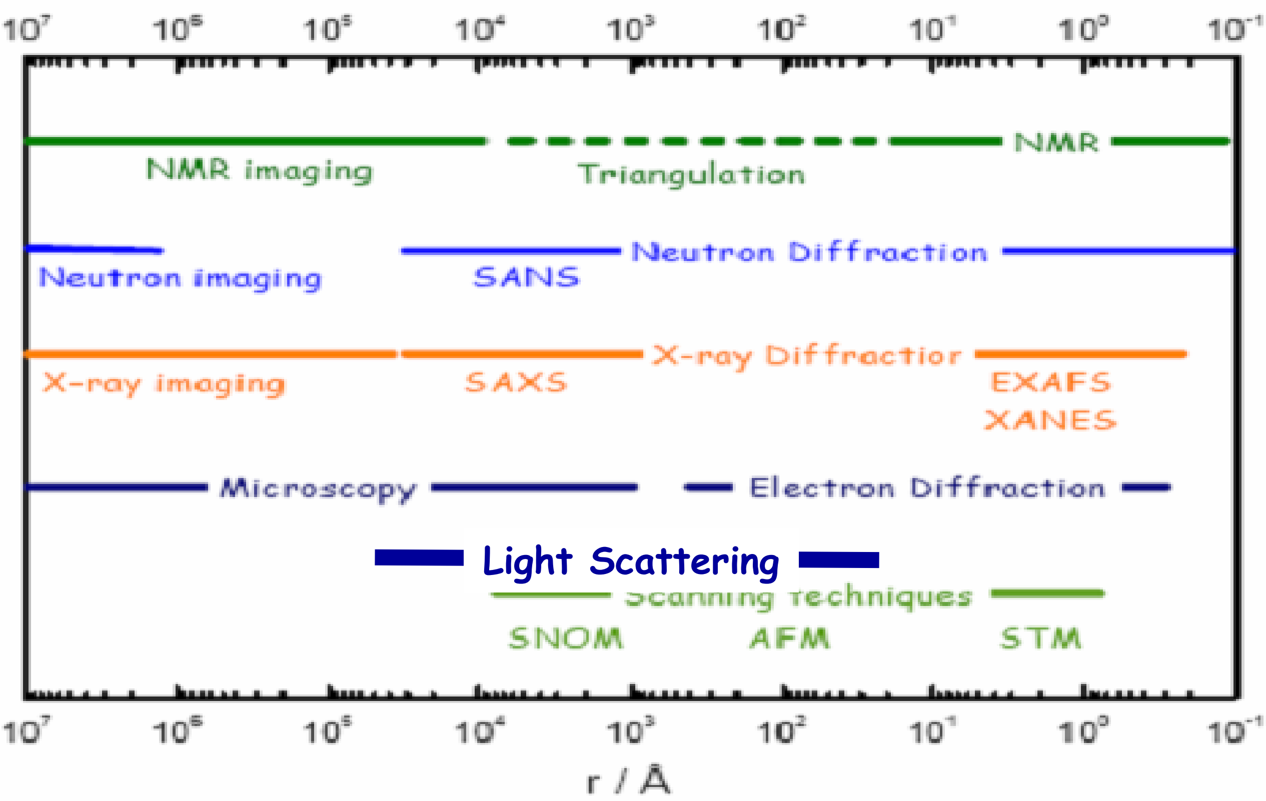
Probability of finding a monomer at a distance r from a given one

$$g(r) \approx \frac{m}{r^3} \approx \frac{1}{rb^2}$$

Pair correlation function for a D-dimensional fractal with $m \sim r^D$

$$g(r) \approx \frac{m}{r^3} \sim r^{D-3}$$

Scattering provides ensemble average information over wide range of scales

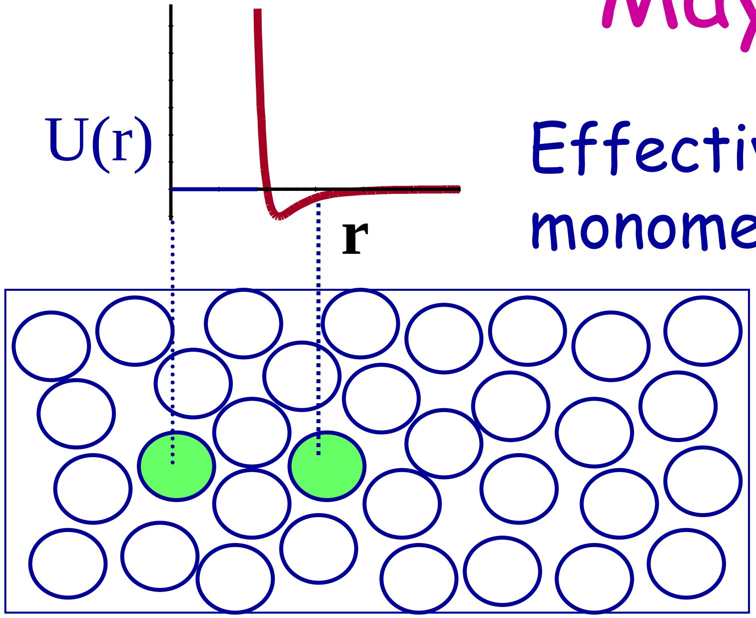


Alan Hurd

Summary of Ideal Chains

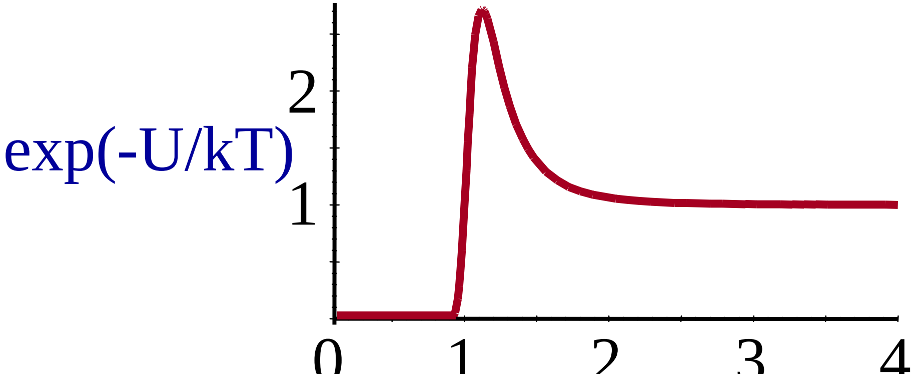
- No interactions except along the chain
- Equivalent Kuhn chain
- Mean square end-to-end: $\langle R^2 \rangle = Nb^2$
- Mean squared gyration radius: $\langle R_g^2 \rangle = \frac{Nb^2}{6}$
- Probability distribution: $P_{3d}(N, \vec{R}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2} \right)$
- Free energy: $F = \frac{3}{2} kT \frac{\vec{R}^2}{Nb^2}$
- Entropic "Hook's Law": $\vec{f} = \frac{3kT}{Nb^2} \vec{R}$
- Pair correlation function: $g(r) = \frac{3}{\pi} \frac{1}{rb^2}$
- Nonlinear elasticity at high forces

Mayer f-function



Effective interactions potential between two monomers in a solution of other molecules.

Relative probability of finding two monomers at distance r

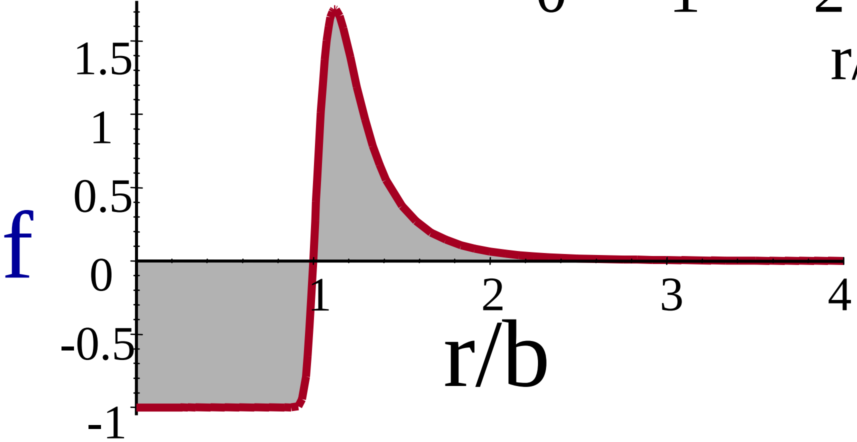


Mayer f-function

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1$$

Excluded volume

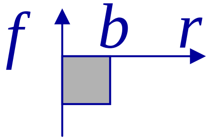
$$v = -\int f(\vec{r})\, d^3 r$$



Classification of Solvents

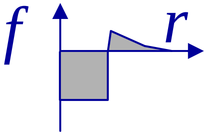
$$v = -\int f(\vec{r})d^3r$$

Athermal, high T



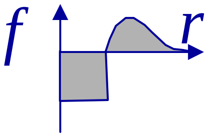
$$v \approx b^3$$

Good solvent, repulsion dominates



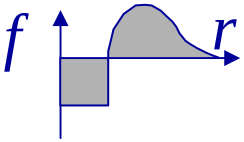
$$0 < v < b^3$$

θ-solvent, repulsion compensates attraction



$$v = 0$$

Poor solvent, attraction dominates



$$v < 0$$

Typically, but not always, repulsion dominates at higher, and attraction -- at lower temperatures.

Pair interaction dominance:

- In ideal coil, $R \sim bN^{1/2}$. Monomer volume fraction $\phi \sim Nb^3/R^3 \sim N^{-1/2} << 1$
- The number of pair contacts $N\phi \sim N^{1/2} >> 1$; pair collisions are important.
- The number of triple contacts $N\phi^2 \sim 1$; they become important only if chain collapses.
- Higher order are unimportant unless strong collapse.